
(12) UK Patent Application (19) GB (11) 2 113 692 A

- (21) Application No 8234989
(22) Date of filing 8 Dec 1982
(30) Priority data
(31) 8138286
(32) 18 Dec 1981
(33) United Kingdom (GB)
(43) Application published
10 Aug 1983
(51) INT CL³
C08C 19/06 1/14
(52) Domestic classification
C3J AK
C3L BC BK
C3W 213 213C
U1S 1363 3017 3026 3028
3066 C3J C3L
(56) Documents cited
None
(58) Field of search
C3J
C3L
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(54) Epoxidized *cis* 1,4-polyisoprene rubber

(57) A method of making epoxidized *cis* 1,4-polyisoprene rubber from natural or synthetic *cis* 1,4-polyisoprene latex comprises reacting the rubber latex stabilised against coagulation by a non-ionic surfactant, with performic acid or peracetic acid formed *in situ*, coagulating the latex by heating to a temperature above the cloud-point of the surfactant, adding base to the rubber, and thoroughly washing the coagulum to remove substantially all residual reactants and modified non-rubbers. The method is adapted for operation on a commercial scale with minimal side reactions and production of rubber having useful vulcanizate properties.

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SPECIFICATION

A method of making epoxidized *cis* 1,4-polyisoprene rubber

5 This invention relates to the manufacture of epoxidized *cis* 1,4-polyisoprenes. In particular it relates to the manufacture of epoxidized natural rubber which has improved vulcanizing characteristics and vulcanizate properties by a method which is adapted for operation on a commercial scale. 5

It has been known for many years that natural rubber can be reacted with peroxides to form epoxy rubber. Early synthesis of such epoxidized materials involved treating rubber with peracids but more recent work 10 has shown that epoxidation can be carried out by generating the peracid *in situ*. Epoxidized rubber vulcanizates are potentially useful materials, they exhibit low gas permeability, high oil resistance, increased glass transition temperatures and improved wet skid resistance compared to the unmodified rubber. These changes are of commercial value. Epoxidized natural rubber, like natural rubber undergoes strain 15 crystallization and hence has good strength properties. In the past exploitation of these properties has been prevented by the occurrence of side reactions in the epoxidation procedure and difficulties arising in scaling up from experimental laboratory synthesis to commercial manufacture. 15

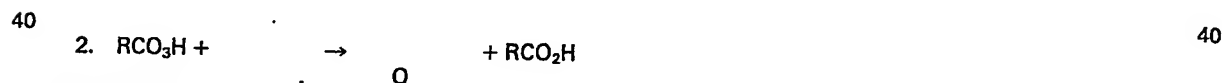
Three main types of side reaction product have been noted under different conditions, carboxyl and hydroxyl pendent groups and saturated furan rings. These side reactions give products with inferior properties, but, by carrying out the epoxidation under carefully controlled conditions it is possible to obtain 20 high yields of epoxidized rubber. 20

Epoxidation of synthetic *cis* 1,4-polyisoprene in solution has been reported but the vulcanizate properties proved similarly disappointing. We are not aware of any proposal to epoxidize synthetic *cis* 1,4-polyisoprene latex. 20

The present invention is based on a technique which combines a synthetic method which produces zero or 25 very low levels of side reactions with a processing method adapted for large scale use to give epoxidized rubber from which vulcanizates having good properties can be prepared. The processing technique removes from the epoxidized rubber non-rubber materials which have a deleterious effect on vulcanizate properties. 25

The present invention accordingly provides a method of making epoxidized rubber which method comprises treating a natural or synthetic *cis* 1,4-polyisoprene latex, which has been stabilized against 30 coagulation with a non-ionic surfactant, with hydrogen peroxide and formic or acetic acid to form *in situ* the corresponding peracid, whereby the rubber is epoxidized to a predetermined extent and subsequently recovering the epoxidized rubber by heating the latex to a temperature above the cloud point of the non-ionic surfactant to coagulate the rubber, before and/or after coagulation adding base to the rubber and subsequently washing the coagulum to remove substantially all residual free acid, residual peroxide, 35 peroxide modified non-rubbers and surfactant from the rubber. 35

The epoxidation reaction can be summarized in the following reaction sequence.



where R is H or CH₃.

The first reaction represents the *in situ* formation of the peracid, which is acid catalysed. Formic acid is 45 itself sufficiently strong so that addition of a separate catalyst is not generally employed. However, acetic acid is a much weaker acid and when it is used it is desirable to include in the reaction system a catalytic amount of a strong acid to prevent the rate of formation of the peracid unduly restricting the overall 45 epoxidation rate. Suitable strong acids include sulphuric acid and *p*-toluene sulphonc acid but such acids in solution also catalyse degradation of the epoxide reaction product. Accordingly, the proportion of these 50 acids will be selected to achieve a practical compromise between the desirable and undesirable catalytic effects. This problem can be solved by using a resin bound strong acid e.g. sulphonated polystyrene as catalyst. The precise amount or concentration of such catalyst acids can be selected within the criteria set out above. 50

The reaction between the peracid and the rubber takes place adequately fast without catalysis. It appears 55 that the main rate limiting factor is the instantaneous concentration of the peracid although when high degrees of epoxidation are achieved the rate may towards the end of the reaction become dependent on the availability of unreacted double bonds. 55

The preferred *cis* 1,4-polyisoprene starting material is a natural rubber latex. The latex can be fresh or preserved. The dry rubber content (drc) of the latex will normally be in the range 15 to 60% by weight of the 60 latex. Field latex typically has a drc from 20 to 40% and more usually 25 to 30%. Use of a latex having a solids content below that of field latex is not preferred because of the slow rate of epoxidation. For synthetic *cis* 1,4-polyisoprene the starting material is the latex, which is commercially available with dry rubber contents in the range 60 to 65% by weight of the latex. To avoid latex instability during reaction, the drc of the reaction mixture will usually be less than 60% by weight. Very high drc latices may be deliberately diluted to ensure 65 this. 65

The amount of hydrogen peroxide used in the reaction to form the peracid *in situ* depends mainly on the desired degree of epoxidation. Typically the desired degree of epoxidation will be from 5 to 75% of the theoretical maximum and these figures correspond to 2.5 to 37.5% of H_2O_2 by weight on the drc of the latex assuming 100% conversion of H_2O_2 to epoxide. In practice 100% conversion is rarely achieved because of peracid and/or hydrogen peroxide decomposition which is catalysed by heavy metal ions present in the latex. The decomposition can be minimised by employing short reaction times and by using chelating agents.

In practice conversions in excess of 90% of theory are possible despite the loss of epoxidizing reagent. The maximum amount of H_2O_2 required will generally be about three times the theoretical molar equivalent.

Larger amounts are uneconomic and make the reaction difficult to control. Use of more than the theoretical minimum is desirable to allow for losses and to ensure completion of the reaction within a suitable time. For epoxidation to 50% the amount of hydrogen peroxide used will typically be from 0.25 to 1.5 parts by weight of H_2O_2 per part by weight of dry rubber. The concentration of hydrogen peroxide in the aqueous phase (i.e. excluding the rubber) will depend on the drc of the latex employed.

The amount of formic or acetic acid will usually be from about 3 to about 10% by weight on the aqueous phase and from 0.15 to 0.5 moles of acid per mole of hydrogen peroxide. When a strong catalytic acid is employed the amount will typically be about 0.05 of a mole per mole of acetic acid. Inclusion of small amounts of suitable chelating agents can reduce the rate of unwanted decomposition of peracid/hydrogen peroxide by metal ions. Suitable chelating agents include 8-hydroxyquinoline and picolinic acid salts e.g. potassium tetradipicolinate, often in conjunction with one or more sodium phosphates and difunctional esters. They suppress the concentration of free heavy metal ions, especially those of iron, nickel and copper, which occur naturally in natural rubber latex or are present as a result of contamination during tapping, bulking, storage etc. The amount of chelating agent necessary is small, typically 10 to 500 ppm by weight on the aqueous phase.

The latex is stabilized against coagulation under acid conditions by inclusion of a non-ionic surfactant. A wide range of non-ionic surfactants including alkanolamides and esters can be used but alkylene oxide condensates with lipophilic residues are particularly appropriate. The lipophilic residue can be a long chain alkyl phenol e.g. nonyl phenol, or a long chain alcohol, amine or carboxylic acid. The alkylene oxide will usually be ethylene oxide or propylene oxide and usually the polyether chain will contain from about 18 - 30 alkylene oxide units although longer chains e.g. up to 75 alkylene oxide units can sometimes be used. These types of non-ionic surfactant are readily available commercially. To be effective in this invention the cloud point of the non-ionic surfactant in the reaction medium, must be above the temperature at which the reaction is carried out (see below). At temperatures above the cloud point the surfactant loses its ability to stabilize the latex, causing undesirable premature coagulation. Advantage is however taken of this property of the surfactants to effect coagulation after completion of the epoxidation reaction. To provide a satisfactory safety margin the cloud point is preferably at least 10°C higher than the reaction temperature. Because the latex is eventually coagulated by heat, the cloud point of the surfactant will usually be less than the boiling temperature of the latex. Typically the surfactants used in the invention have cloud points in the range 60 to 95°C provided that the minimum is at least 10°C higher than the reaction temperature.

The non-ionic surfactant is used in an amount sufficient to maintain the stability of the latex during the reaction. The amount or concentration in any particular case depends on the specific surfactant chosen but will generally be in the range 0.5 to 8% and more usually from 1 to 5% by weight on the dry rubber content of the latex.

The reaction temperature can be ambient temperature, which is typically about 15 to 20°C in temperate climates but may be from 30 to 35°C in tropical rubber-producing countries, or moderately elevated temperature. Temperatures above 80°C will not normally be used because at such elevated temperatures side reactions leading to loss or degradation of the product become more significant and it is difficult to maintain stability of the latex. Within this broad range the reaction rate increases with temperature. Typical reaction temperatures are in the range 30 to 65°C.

The reaction time depends mainly on the desired degree of epoxidation, the concentration of the reagents and temperature. As a general guide reaction times are typically between 2 and 24 hours.

After completion of the epoxidation reaction the solid rubber is obtained by coagulation, purification and drying. The invention includes the step of thermally coagulating the latex. This can readily be carried out by heating the latex to a temperature above the cloud point of the non-ionic surfactant.

Typically the latex will be heated to a temperature in the range 80 to 100°C although lower temperatures e.g. between 50 and 80°C may be effective where the reaction is carried out at correspondingly lower temperature and the surfactant has a suitably lower cloud point. Ionic salts e.g. sodium chloride, ammonium sulphate, may be added to the latex to lower the effective cloud point of the surfactant and hence the temperature of coagulation. Typically the ionic salt is used at 10% by weight on the drc of the latex. We have found that other commonly used coagulation techniques are ineffective or inefficient leaving a relatively large proportion of rubber in the serum, or too expensive to be commercially viable. Specifically, addition of further acid to coagulate the latex is ineffective because of the presence of non-ionic surfactant.

A very important feature of the invention is that the rubber is "purified". We have found that residues from the epoxidation reaction cause poor vulcanizing and vulcanizate properties even though the epoxidized rubber is free from secondary reaction products. Simple water washing of the coagulum is ineffective in

removing such residues. In this invention the rubber is treated with base and subjected to a washing cycle. The treatment can be carried out either wholly or partly before coagulation by adding a base to the latex. Suitable bases include ammonia, sodium or potassium hydroxide, or sodium or potassium hydrogen carbonate or carbonate.

- 5 Alternatively the treatment with base can be effected after coagulation by first creping the coagulum or passing it through a hammer mill or extruder, so as to give the rubber a high relative surface area, and then working it in base. If the treatment with base is carried out prior to coagulation then a further base treatment may be necessary during washing. 5

- The number or extent of the washing steps, crepe mill and/or soaking will depend on the particular conditions employed in the epoxidation reaction e.g. amount of surfactant used, and level of residual peroxide. The intent is to remove substantially all residual free acid, the surfactant, residual peroxide (as H_2O_2 or peracid) and any peroxide modified non-rubbers. The rubber is considered to be free from residual acid and excess base used in the above treatments when the equilibrium pH of water in contact with the rubber is between about 7 and about 9 and preferably from 7.5 to 8.5. Rubber which has a pH below 7 but is free from other residues after washing and drying may be usefully utilized by addition of base at the compounding stage to bring the pH of the rubber to the optimum value. This is normally carried out either on a mill or in an internal mixer at the start of the mix cycle. Rubber treated in this way has similar vulcanizing and vulcanizate properties to that correctly treated during the work-up procedure. 10 15

- The epoxidation reaction effectively removes and/or destroys the natural antioxidants present in natural rubber latex and these should preferably be replaced, during the work-up procedure, or towards the end of the epoxidation reaction, preferably in an amount of 0.1 to 2 phr. Suitable antioxidants are those generally employed to stabilize raw rubbers, including non-staining phenolics or amines. 20

After washing and soaking the rubber is finally dried, temperatures from ambient to 110°C may be employed.

- 25 The improvement in properties obtained by epoxidizing rubbers as described is apparent in vulcanizates produced subsequently from the modified rubber. A wide range of conventional vulcanizing systems can be used. 25

- The vulcanized rubbers show improved oil resistance, reduced gas permeability, increased damping, improved wet skid resistance and other beneficial properties while retaining the high strength properties of natural rubber. Our initial results indicate that similar improved properties are obtained from synthetic *cis* 1,4-polyisoprene. 30

The following Examples illustrate the invention, phr means parts by weight per hundred parts by weight of rubber, and drc means dry rubber content.

35 Example 1 35

- Natural rubber latex (900g, 30% drc) as either fresh field latex or diluted concentrate was stabilized with a non-ionic alkoxylate surfactant (2 phr) and the latex acidified with 98% formic acid (0.20 moles per mole of isoprene units). The stirred latex was warmed to 60°C and hydrogen peroxide (0.74 moles per mole of isoprene units) added. The temperature was maintained at 60°C for 23 hours, 1 phr of 2,5-di-tertiarypentyl hydroquinone was added as an aqueous dispersion and the latex heated for a further 1 hour, after which time 50 mole % epoxidized natural rubber latex was obtained. This Example was repeated using about 330 kg of natural rubber latex (30% drc corresponding to ca. 100 kg dry rubber) to give 50 mole % epoxidized natural rubber latex. 40

45 Example 2 45

- Natural rubber latex (900g, 30% drc) was stabilized with a non-ionic alkoxylate surfactant (5 phr) and acidified with 98% formic acid (0.3 moles per mole of isoprene units). The stirred latex was warmed to 50°C and hydrogen peroxide (3.0 moles per mole of isoprene units) added slowly. The temperature was maintained at 50°C for 2.5 hr, after which time 50 mole % epoxidized natural rubber latex was obtained. 50

50 Example 3 50

- Synthetic *cis* 1,4-polyisoprene latex (750g, 60% drc) was stabilized with a non-ionic alkoxylate surfactant (3 phr) and the latex acidified with 90% formic acid (0.25 moles per mole of isoprene units). The stirred latex was warmed to 50°C and hydrogen peroxide (0.75 moles per mole of isoprene units) added slowly. The temperature was maintained at 50°C for 4.5 hr, after which time 25 mole % epoxidized synthetic *cis* 1,4-polyisoprene latex was obtained. 55

Example 4

- (a) Samples of epoxidized latex produced by Examples 1 to 3 were coagulated by the passage of steam, the coagulum passed three times through a crepe mill with water washing and the rubber dried at 80°C (Comparative Example). 60

- (b) Samples of epoxidized latex produced by Examples 1 to 3 were partially neutralized (pH 5) with a base, sodium chloride (10 phr) added and steam coagulated. The coagulum was passed three times through a crepe mill with water washing, crumbled soaked in 0.1M aqueous sodium carbonate solution, washed, soaked in 0.2% thiourea solution, and dried at 80°C. 65

(c) Samples of epoxidized latex produced by Examples 1 to 3 were partially neutralized to pH 6 with ammonia and coagulated by heat. The coagulum was washed with water, soaked in 0.1% thiourea and dried at 80°C. Subsequently, it was mixed with sodium carbonate to bring the pH up to 8.0.

(d) Samples of epoxidized latex produced by Examples 1 to 3 were neutralized to pH 7 to 8 and coagulated by heat. The coagulum was washed with water on a crepe mill, soaked in sodium hydrogen carbonate, washed and dried at 80°C.

Example 5

Samples of 50% epoxidized natural rubber from Examples 4 (a), (b), (c) and (d) were made up into 10 formulations as follows:-

Formulations		I	II
15	50% Epoxidized natural rubber	100	100
	High abrasion furnace black	-	40
	Aromatic process oil	-	4
	Zinc Oxide	5	5
	Stearic acid	2	2
20	Antioxidant	2	2
	Sulphur	1.5	1.5
	2-Morpholinothiobenzthiazole	1.5	1.5

The following Table I illustrates the improvement in properties obtained on epoxidizing natural rubber. The need to substantially remove deleterious non-rubbers is also demonstrated, inadequate washing procedure (Example 4(a)), adequate washing (Example 4(b) and 4(d)), inadequate removal of acid (Example 4(c)) and its correction by the addition of base during the mixing cycle.

Within experimental error, natural rubber of a given degree of epoxidation produced according to the invention had the same measured properties irrespective of the epoxidation reaction conditions (Examples 1 and 2) or the detail of the neutralization and washing (Examples 4(b) and 4(d)) provided it was adequate (cf. Example 4(a)).

TABLE 1
Comparison of properties and work-up procedures

5	Work-up procedure Formulation Mooney Scorch (ISO 667) t + 5 (120°C) min Monsanto Rheometer (150°C) (ISO 3417) t + 2 (min) t opt (min) ΔT (in lb) Vulcanizate Properties (MPa) (ISO 37) 20 M100 M300% TS EB% Hardness (IRHD) 25 (ISO 48) Dunlop Resilience (23°C) (BS 903 A8) Fatigue (kcs) (ISO/DP 6943) 30 0-100% 50-150% Swelling, % volume increase 23°C/17 days (ISO 1817) 35 ASTM No. 1 oil ASTM No. 3 oil Air Permeability cm ² sec ⁻¹ atm ⁻¹ (ISO 1399) 40 Akron Abrasion (BS 903 A9) mg loss per 500 rev. Relative wet skid resistance* 45	Natural Rubber (NR)	50% Epoxidized				(NR) 5
			4(a)	4(b)	4(c)	4(d)	
	I	I	I	I	II	II	
10	t + 5 (120°C) min Monsanto Rheometer (150°C) (ISO 3417)	60	5	27	7	23	10
15	t + 2 (min) t opt (min) ΔT (in lb) Vulcanizate Properties (MPa) (ISO 37)	15 25 32	1.5 6.0 43	6.0 17 34	3.5 23 59	4.3 16 62	15
20	M100 M300% TS EB% Hardness (IRHD)	0.74 1.58 27.1 740	2.39 6.31 9.0 375	0.68 1.44 25.5 730	2.3 11.2 18.2 410	2.4 12.5 25.8 505	20
25	(ISO 48) Dunlop Resilience (23°C) (BS 903 A8) Fatigue (kcs) (ISO/DP 6943)	41 90%	55 4%	42 33%	72 23%	68 23%	25
30	0-100% 50-150% Swelling, % volume increase 23°C/17 days (ISO 1817)	58 985	81 100	165 555	94 401	274 809	30
35	ASTM No. 1 oil ASTM No. 3 oil Air Permeability cm ² sec ⁻¹ atm ⁻¹ (ISO 1399)	74 261 7.6	1.0 16 1.2	0.8 14 0.9	0 3 5.8	0 2 5.0	35
40	Akron Abrasion (BS 903 A9) mg loss per 500 rev. Relative wet skid resistance*	244 100	37 121	21 156	20 133	10 140	40
45							45

* Measured on a commercial pendulum apparatus (1 m/sec) The natural rubber vulcanizate was taken as 100 and the other results rated accordingly.

50 Example 6

Natural rubber latex (2266g, 30% drc) was stabilized with a non-ionic alkoxyated surfactant (3 phr) and acidified with glacial acetic acid (0.2 moles per mole isoprene units) and sulphuric acid (0.05 moles per mole of acetic acid). The stirred latex was warmed to 50°C and hydrogen peroxide (0.38 moles per mole of isoprene units) added. After 24h at 60°C partially epoxidized natural rubber latex was obtained. The latex was coagulated with steam, and the coagulum creped, soaked in alkali, washed to pH 8 and dried.

CLAIMS

1. A method of making epoxidized *cis* 1,4-polyisoprene rubber, which method comprises treating a natural or synthetic *cis* 1,4-polyisoprene latex, which has been stabilized against coagulation with a non-ionic surfactant, with hydrogen peroxide and formic or acetic acid to form *in situ* the corresponding per-acid, whereby the rubber is epoxidized to a predetermined extent and subsequently recovering the epoxidized rubber by heating the latex to a temperature above the cloud point of the non-ionic surfactant to coagulate the rubber, before and/or after coagulation adding base to the rubber and subsequently washing the coagulum to remove substantially all residual free acid, residual peroxide, peroxide-modified

non-rubbers and surfactant from the rubber.

2. A method as claimed in claim 1, wherein the rubber is epoxidized to from 5% to 75% of the theoretical maximum.

3. A method as claimed in claim 1 or claim 2, wherein there are used from 0.25 to 1.5 parts by weight of hydrogen peroxide per part by weight of dry rubber.

4. A method as claimed in any one of claims 1 to 3, wherein the formic or acetic acid is used in a concentration of about 3% to about 10% on the aqueous phase and in an amount of from 0.15 to 0.5 moles of acid per mole of hydrogen peroxide.

5. A method as claimed in any one of claims 1 to 4, wherein the non-ionic surfactant is an alkylene oxide condensate with a lipophilic residue, having a cloud point of from 60°C to 95°C.

6. A method as claimed in any one of claims 1 to 5, wherein the base used is ammonia, sodium or potassium hydroxide, or sodium or potassium hydrogen carbonate or carbonate.

7. A method as claimed in any one of claims 1 to 6, wherein the rubber coagulum is creped and then soaked in the base prior to washing.

8. A method as claimed in any one of claims 1 to 7, wherein the rubber coagulum is washed until the equilibrium pH of water in contact with the rubber is from 7 to 9.

9. A method as claimed in claim 8, wherein the rubber coagulum is washed until the equilibrium pH of water in contact with the rubber is from 7.5 to 8.5.

10. A method as claimed in any one of claims 1 to 9, wherein an antioxidant is added during or after the epoxidation reaction to stabilize the epoxidized rubber.

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